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*PROCESS FOR LIMITING HYDROCARBON
A CONVERSION CATALYST*
HYDROCARBON CONVERSION CATALYST COMPOSITION

AND PROCESSES THEREFOR AND THEREWITH

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FIELD OF THE INVENTION

This invention relates to a composition useful for converting a hydrocarbon to a C₆ to C₈ aromatic hydrocarbon and an olefin, to a process for producing the composition, and to a process for using the composition for converting a hydrocarbon to a C₆ to C₈ aromatic hydrocarbon and an olefin (hydrocarbon conversion process).

BACKGROUND OF THE INVENTION

It is well known to those skilled in the art that aromatic hydrocarbons and olefins are each a class of very important industrial chemicals which find a variety of uses in petrochemical industry. It is also well

known to those skilled in the art that catalytically cracking gasoline-range hydrocarbons produces lower olefins such as, for example, propylene; and aromatic hydrocarbons such as, for example, benzene, toluene, and xylenes (hereinafter collectively referred to as BTX) in the presence of catalysts which contain a zeolite. The product of this catalytic cracking process contains a multitude of hydrocarbons including unconverted C_5+ alkanes; lower alkanes such as methane, ethane, and propane; lower alkenes such as ethylene and propylene; C_6 - C_8 aromatic hydrocarbons; and C_9+ aromatic compounds which contain 9 or more carbons per molecule. Recent efforts to convert gasoline to more valuable petrochemical products have therefore focused on improving the conversion of gasoline to olefins and aromatic hydrocarbons by catalytic cracking in the presence of zeolite catalysts. For example, a gallium-promoted zeolite ZSM-5 has been used in the so-called Cyclar Process to convert a hydrocarbon to BTX.

Olefins and aromatic hydrocarbons can be useful feedstocks for producing various organic compounds and polymers. However, a zeolite catalyst is generally deactivated in a rather short period, especially in a high sulfur and/or high polyaromatic environment, because of depositions of carbonaceous material, generally coke, on the surface of the catalyst.

Moreover, the BTX purity in the product is generally not desirably high.

Therefore, development of a catalyst and a process for converting hydrocarbons to the more valuable olefins and BTX and for reducing coke deposition would be a significant contribution to the art and to the economy.

SUMMARY OF THE INVENTION

5 An object of this invention is to provide a catalyst composition which can be used to convert a hydrocarbon to a C_6 to C_8 aromatic hydrocarbon and an olefin. Also an object of this invention is to provide a process for producing the catalyst composition. Another object of this invention is to provide a process which can employ the catalyst composition to convert a
10 hydrocarbon to an olefin and a C_6 to C_8 aromatic hydrocarbon. An advantage of the catalyst composition is that it suppresses the deposition of coke during a hydrocarbon conversion process. Other objects and advantages will become more apparent as this invention is more fully disclosed hereinbelow.

 According to a first embodiment of the present invention, a
15 composition which can be used as a catalyst for converting a hydrocarbon or a hydrocarbon mixture to an olefin and a C_6 to C_8 aromatic hydrocarbon is provided. The composition comprises a zeolite, optionally a binder, and at least one metal or element selected from the group consisting of Group IA, Group IIA, Group IIIA, Group IVA, Group VA, Group IIB, Group IIIB, Group IVB,
20 Group VIB, of the Periodic Table of the Elements, CRC Handbook of

Chemistry and Elements, 67th edition, 1986-1987 (CRC Press, Boca Raton, Florida), and combinations of two or more thereof.

According to a second embodiment of the present invention, a process which can be used for producing a catalyst composition is provided.

5 The process comprises the steps: (1) optionally contacting a zeolite with steam whereby a steamed zeolite is formed; (2) optionally contacting a zeolite or the steamed zeolite with an acid in an amount and under a condition effective to produce an acid-leached zeolite; (3) combining a zeolite, which can also be the steamed zeolite or the acid-leached zeolite, with a promoter, and optionally a
10 binder under a condition sufficient to incorporate the promoter into the zeolite to produce a modified zeolite; and (4) heat-treating the modified zeolite to produce a promoted zeolite wherein the promoter is a metal or element selected from the group consisting of Group IA, Group IIA, Group IIIA, Group IVA, Group VA, Group IIB, Group IIIB, Group IVB, Group VIB, of the Periodic
15 Table of the Elements, CRC Handbook of Chemistry and Elements, 67th edition, 1986-1987 (CRC Press, Boca Raton, Florida), and combinations of two or more thereof.

According to a third embodiment of the present invention, a process which can be used for converting a hydrocarbon or a hydrocarbon
20 mixture to an olefin and a C₆ to C₈ aromatic hydrocarbon is provided which

comprises, consists essentially of, or consists of, contacting a fluid which comprises at least one saturated hydrocarbon with a catalyst composition, which can be the same as disclosed above in the first embodiment of the invention, under a condition effective to convert a hydrocarbon to an olefin and an aromatic hydrocarbon containing 6 to 8 carbon atoms per molecule.

DETAILED DESCRIPTION OF THE INVENTION

The catalyst composition of the first embodiment of the present invention can comprise, consist essentially of, or consist of a zeolite, a promoter, and optionally a binder. According to the present invention the weight ratio of binder to zeolite can be any ratio and can be in the range of from about 1:20 to about 20:1, preferably about 1:10 to about 10:1, and most preferably about 1:7 to about 5:1. The promoter is a metal or element selected from the group consisting of Group IA, Group IIA, Group IIIA, Group IVA, Group VA, Group IIB, Group IIIB, Group IVB, Group VIB, of the Periodic Table of the Elements, and combinations of two or more thereof. The term "promoter" refers to a compound, a metal, or an element that, when incorporated in a zeolite, can suppress coke formation, or enhance olefin production, or both, in a hydrocarbon conversion process. The term "metal or element" used herein also includes a compound of the metal or element. For the interest of simplicity, any references to "metal" in the application, unless

otherwise indicated, will include the elements listed above and a compound of any of the elements.

The weight ratio of each promoter to zeolite can be any ratio as long as the ratio can suppress the coke formation during a hydrocarbon conversion process. Generally, the ratio can be in the range of from about 0.01:1 to about 1:1, preferably about 0.03:1 to about 1:1, and most preferably 0.04:1 to 0.5:1.

Any binders known to one skilled in the art for use with a zeolite are suitable for use herein. Examples of suitable binders include, but are not limited to, a clay such as kaolinite, halloysite, vermiculite, chlorite, attapulgite, smectite, montmorillonite (bentonite), illite, saconite, sepiolite, and palygorskite; aluminas such as for example α -alumina and γ -alumina; silicas; alumina-silica; aluminum phosphate; aluminum chlorohydrate; and combinations of two or more thereof. Because these binders are well known to one skilled in the art, description of which is omitted herein. The presently preferred binder, if employed, is silica because it is readily available.

The composition can further be characterized by having the following physical characteristics: a surface area as determined by the BET method using nitrogen in the range of from about 300 to about 600, preferably 350 to 500 m²/g; a pore volume in the range of from about 0.4 to about 0.8,

preferably about 0.5 to about 0.75, and most preferably 0.6 to 0.75 ml/g; an average pore diameter in the range of from about 70 to about 300, preferably about 100 to about 250, and most preferably 125 to 200 Å; and a porosity of more than about 50%.

5 According to the present invention, any compound containing a metal or element selected from the group consisting of Group IA, Group IIA, Group IIIA, Group IVA, Group VA, Group IIB, Group IIIB, Group IVB, Group VIB, of the Periodic Table of the Elements, and elements in these groups, and combinations of two or more thereof can be used as promoter.

10 Illustrated hereinbelow are some examples of suitable promoters.

 Any zinc-containing compounds, such as, for example zinc spinels, which can, when incorporated into a zeolite, reduce coke formation in a hydrocarbon conversion process can be used in the present invention.

 Examples of suitable zinc-containing compounds include, but are not limited
15 to, zinc titanate, zinc silicate, zinc borate, zinc fluorosilicate, zinc fluorotitanate, zinc molybdate, zinc chromate, zinc tungstate, zinc zirconate, zinc chromite, zinc aluminate, zinc phosphate, zinc acetate dihydrate, diethylzinc, zinc 2-ethylhexanoate, and combinations of two or more thereof.

 Also any titanium-containing compounds that, when incorporated
20 into a zeolite, reduce coke formation in a hydrocarbon conversion process can

be employed in the invention. Examples of suitable titanium-compounds include, but are not limited to, titanium zinc titanate, lanthanum titanate, titanium tetramides, titanium tetramercaptides, titanium chloride, titanium oxalate, zinc titanate, tetraisopropyl titanate, tetra-n-butyl titanate, tetrakis(2-ethylhexyl) titanate, titanium tetramethoxide, titanium dimethoxydiethoxide, titanium tetraethoxide, titanium tetra-n-butoxide, titanium tetrahexyloxide, titanium tetradecyloxide, titanium tetraeicosyloxide, titanium tetracyclohexyloxide, titanium tetrabenzoyloxide, titanium tetra-p-tolyloxide, titanium tetraphenoxide, and combinations of two or more thereof.

Similarly, examples of suitable magnesium-containing compounds include, but are not limited to, magnesium silicate, magnesium nitrate, magnesium acetate, magnesium acetylacetoante, magnesium chloride, magnesium molybdate, magnesium hydroxide, magnesium sulfate, magnesium sulfide, magnesium titanate, magnesium tungstate, magnesium formate, magnesium bromide, magnesium bromide diethyl etherate, magnesium fluoride, dibutyl magnesium, magnesium methoxide, $\text{Mg}(\text{OC}_2\text{H}_5)_2$, $\text{Mg}(\text{OSO}_2\text{CF}_3)_2$, dipropyl magnesium, and combinations of two or more thereof.

Generally any silicon-containing compounds which are effective to suppress coke formation on a zeolite in a hydrocarbon conversion process

can be used in the present invention. Examples of suitable silicon-containing compounds can have a formula of $(R)(R)(R)Si-(O_mSi(R)(R))_nR$ wherein each R can be the same or different and is independently selected from the group consisting of hydrogen, alkyl radicals, alkenyl radicals, aryl radicals, alkaryl radicals, aralkyl radicals, and combinations of any two or more thereof; m is 0 or 1; and n is 1 to about 10 wherein each radical can contain 1 to about 15, preferably 1 to about 10 carbon atoms per radical. Specific examples of such compounds include, but are not limited to, silicon-containing polymers such as poly(phenylmethylsiloxane), poly(phenylethylsiloxane), poly(phenylpropylsiloxane), hexamethyldisiloxane, decamethyltetrasiloxane, diphenyltetramethyldisiloxane, and combinations of any two or more thereof. Other silicon-containing compounds include organosilicates such as, for example, tetraethyl orthosilicate. A number of well known silylating agents such as trimethylchlorosilane, chloromethyldimethylchlorosilane, N-trimethylsilylimidazole, N,O-bis(trimethylsilyl)acetamide, N-methyl-N-trimethylsilyltrifluoroacetamide, t-butyltrimethylsilylimidazole, N-trimethylsilylacetamide, methyltrimethoxysilane, vinyltriethoxysilane, ethyltrimethoxysilane, propyltrimethoxysilane, (3,3,3-trifluoropropyl)trimethoxysilane, [3-(2-aminoethyl)aminopropyl]trimethoxysilane, cyanoethyltrimethoxysilane,

aminopropyltriethoxysilane, phenyltrimethoxysilane,
(3-chloropropyl)trimethoxysilane, (3-mercaptopropyl)trimethoxysilane,
(3-glycidoxypropyl)trimethoxysilane, vinyltris(β -methoxyethoxy)silane,
(γ -methacryloxypropyl)trimethoxysilane, vinylbenzyl cationic silane,
5 (4-aminopropyl)triethoxysilane,
[γ -(β -aminoethylamino)propyl]trimethoxysilane,
(γ -glycidoxypropyl)trimethoxysilane,
[β -(3,4-epoxycyclohexyl)ethyl]trimethoxysilane,
(β -mercaptoethyl)trimethoxysilane, (γ -chloropropyl)trimethoxysilane, and
10 combinations of two or more thereof can also be employed. The presently
preferred silicon-containing compounds are tetraethyl orthosilicate and
poly(phenylmethyl) siloxane.

Similarly, any phosphorus-containing compounds that, when
impregnated onto or incorporated into a metal oxide-promoted alumina can be
15 converted into a phosphorus oxide, are capable of reducing coke deposition on
a metal oxide-promoted alumina, as compared to the use of the metal
oxide-promoted alumina only, can be used in the present invention. Examples
of suitable phosphorus-containing compounds include, but are not limited to,
phosphorus pentoxide, phosphorus oxychloride, phosphoric acid, phosphites
20 $P(OR)_3$ such as triethyl phosphite, phosphates $P(O)(OR)_3$ such as triethyl

phosphate and tripropyl phosphate, phosphines $P(R)_3$, and combinations of two or more thereof wherein R is the same as that disclosed above.

Examples of suitable boron-containing compounds include, but are not limited to, boron oxide, boric acid, borane-ammonium complex, boron trichloride, boron phosphate, boron nitride, triethyl borane, trimethyl borane, tripropyl borane, trimethyl borate, triethyl borate, tripropyl borate, trimethyl boroxine, triethyl boroxine, tripropyl boroxine, and combinations of two or more thereof.

Similarly, examples of suitable tin-containing compounds include, but are not limited to, stannous acetate, stannic acetate, stannous bromide, stannic bromide, stannous chloride, stannic chloride, stannous oxalate, stannous sulfate, stannic sulfate, stannous sulfide, and combinations of two or more thereof.

Similarly, examples of suitable zirconium-containing compounds include, but are not limited to, zirconium acetate, zirconium formate, zirconium chloride, zirconium bromide, zirconium butoxide, zirconium *tert*-butoxide, zirconium chloride, zirconium citrate, zirconium ethoxide, zirconium methoxide, zirconium propoxide, and combinations of any two or more thereof.

Suitable molybdenum-containing compounds include, but are not limited to, molybdenum chloride, molybdenum acetate, molybdenum fluoride,

molybdenum oxychloride, molybdenum sulfide, ammonium heptamolybdate and combinations of two or more thereof.

Examples of suitable germanium-containing compounds include, but are not limited to, germanium chloride, germanium bromide, germanium ethoxide, germanium fluoride, germanium iodide, germanium methoxide, and combinations of two or more thereof.

Examples of suitable indium-containing compounds include, but are not limited to indium acetate, indium bromide, indium chloride, indium fluoride, indium iodide, indium nitrate, indium phosphide, indium selenide, indium sulfate, and combinations of two or more thereof.

Examples of suitable lanthanum-containing compounds include, but are not limited to, lanthanum acetate, lanthanum carbonate, lanthanum octanoate, lanthanum fluoride, lanthanum chloride, lanthanum bromide, lanthanum iodide, lanthanum nitrate, lanthanum perchlorate, lanthanum sulfate, lanthanum titanate, and combinations of two or more thereof.

Examples of suitable chromium containing compounds include, but are not limited to, chromium acetate, chromium acetylacetonate, chromium chloride, chromium fluoride, chromium hexacarbonyl, chromium nitrate, chromium nitride, chromium 2,4-pentanedionate, chromium perchlorate,

chromium potassium sulfate, chromium sulfate, chromium telluride, and combinations of two or more thereof.

Other suitable promoter compounds include, but are not limited to, sodium acetate, sodium acetylacetonate, sodium bromide, sodium iodide, sodium nitrate, sodium sulfate, sodium sulfide, potassium acetate, potassium acetylacetonate, potassium bromide, potassium chloride, potassium nitrate, potassium octanoate, potassium phosphate, potassium sulfate, tungsten bromide, tungsten chloride, tungsten hexacarbonyl, tungsten oxychloride, tungsten sulfide, tungstic acid, and combinations of two or more thereof.

Any commercially available zeolite which can catalyze the conversion of a hydrocarbon to an aromatic compound and an olefin can be employed in the present invention. Examples of suitable zeolites include, but are not limited to, those disclosed in Kirk-Othmer Encyclopedia of Chemical Technology, third edition, volume 15 (John Wiley & Sons, New York, 1991) and in W. M. Meier and D. H. Olson, "Atlas of Zeolite Structure Types," pages 138-139 (Butterworth-Heinemann, Boston, Mass., 3rd ed. 1992). Optionally a zeolite can be steam - and/or acid - treated before using the present invention. The presently preferred zeolites are those having medium pore sizes and having the physical characteristics disclosed above. ZSM-5 and similar zeolites that

have been identified as having a framework topology identified as MFI are particularly preferred because of their shape selectivity.

The composition of the present invention can be prepared by combining a zeolite, a promoter, and a binder in the weight ratios disclosed above under any conditions sufficient to effect the production of such a composition.

Generally a zeolite, before a binder is combined with the zeolite, can also be calcined under similar conditions to remove any contaminants, if present, to prepare a calcined zeolite.

A zeolite, whether it has been calcined or contains a binder, can also be treated with steam. The treatment of a zeolite, which can contain a binder, with steam can be carried out in any suitable container or vessel known to one skilled in the art at about 100°C to about 1000°C for about 1 to about 30 hours under any pressure that can accommodate the temperatures to produce a steamed zeolite.

A zeolite, whether it has been steamed or not, can be treated with an acid before the preparation of the present composition. Generally, any organic acids, inorganic acids, or combinations of any two or more thereof can be used in the process of the present invention so long as the acid can reduce the aluminum content in the zeolite. The acid can also be a diluted aqueous

acid solution. Examples of suitable acids include, but are not limited to sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid, formic acid, acetic acid, oxalic acid, trifluoroacetic acid, trichloroacetic acid, p-toluenesulfonic acid, methanesulfonic acid, partially or fully neutralized acids wherein one or more protons have been replaced with, for example, a metal (preferably an alkali metal) or ammonium ion, and combinations of any two or more thereof.

Examples of partially or fully neutralized acids include, but are not limited to, sodium bisulfate, sodium dihydrogen phosphate, potassium hydrogen tartrate, ammonium sulfate, ammonium chloride, ammonium nitrate, and combinations thereof.

Any methods known to one skilled in the art for treating a solid catalyst with an acid can be used in the acid treatment of the present invention. Generally, a zeolite material, whether or not it contains a binder, or has been steamed, can be suspended in an acid solution. The concentration of the zeolite in the acid solution can be in the range of from about 0.01 to about 700, preferably about 0.1 to about 600, more preferably about 1 to about 550, and most preferably 5 to 500 grams per liter. The amount of acid required is the amount that can maintain the solution in acidic pH during the treatment.

Preferably the initial pH of the acid solution containing a zeolite is adjusted to lower than about 7, preferably lower than about 6. Upon the pH adjustment of

the solution, the solution can be subjected to a treatment at a temperature in the range of from about 30°C to about 200°C, preferably about 50°C to about 150°C, and most preferably 70°C to 120°C for about 10 minutes to about 30 hours, preferably about 20 minutes to about 25 hours, and most preferably 30 minutes to 20 hours. The treatment can be carried out under a pressure in the range of from about 1 to about 10 atmospheres (atm), preferably about 1 atm so long as the desired temperature can be maintained. Thereafter, the acid-treated zeolite material can be washed with running water for 1 to about 60 minutes followed by drying, at about 50 to about 1000, preferably about 75 to about 750, and most preferably 100 to 650°C for about 0.5 to about 15, preferably about 1 to about 12, and most preferably 1 to 10 hours, to produce an acid-leached zeolite. Any drying method known to one skilled in the art such as, for example, air drying, heat drying, spray drying, fluidized bed drying, or combinations of two or more thereof can be used.

It should be noted that, a zeolite can be acid-leached before it is treated with steam.

The dried, acid-leached zeolite can be heat-treated: either heated with steam or calcined under a condition known to those skilled in the art.

Generally such a condition can include a temperature in the range of from about 250 to about 1,000, preferably about 350 to about 750, and most preferably 450

to 650°C and a pressure in the range of from about 0.5 to about 50, preferably about 0.5 to about 30, and most preferably 0.5 to 10 atmospheres (atm) for about 1 to about 30 hours, preferably about 2 to about 20 hours, and most preferably 3 to 15 hours.

5 A zeolite, a calcined zeolite, or a calcined zeolite-binder mixture, can be treated with a compound containing an exchangeable ammonium ion to prepare an ammonium-exchanged zeolite. Whether a zeolite is calcined or contains a binder, the process or treatment in the second embodiment is the same for each. For the interest of brevity, only a zeolite is described
10 hereinbelow. Examples of suitable ammonium-containing compounds include, but are not limited to, ammonium sulfate, ammonium chloride, ammonium nitrate, ammonium bromide, ammonium fluoride, and combinations of any two or more thereof. Treatment of the zeolite replaces the original ions such as, for example, alkali or alkaline earth metal ions of the zeolite, with predominantly
15 ammonium ions. Techniques for such treatment are well known to one skilled in the art such as, for example, ion exchange of the original ions. For example, a zeolite can be contacted with a solution containing a salt of the desired replacing ion or ions. Because ion exchange in zeolite is well known to one skilled in the art, description of which is omitted herein.

In the second embodiment of the invention, a zeolite which could have been steamed and/or acid-leached, in a desired ionic form, regardless whether calcined or not, can be combined with a binder and a promoter at about 15 to about 100°C under atmospheric pressure, generally in a liquid such as water or a hydrocarbon, by any means known to one skilled in the art such as stirring, blending, kneading, or extrusion, following which the resulting mixture can be dried in air at a temperature in the range of from about 20 to about 800°C, for about 0.5 to about 50 hours under any pressures that accommodate the temperatures, preferably under atmospheric pressure.

Thereafter, mixture can be further heat-treated at a temperature in the range of from about 200 to 1000°C, preferably about 250 to about 750°C, and most preferably 350 to 650°C for about 1 to about 30 hours to prepare the present composition. The heat treatment can be carried out by air calcination or steam.

The composition can also be produced by contacting a zeolite with a promoter compound and optionally a binder, in a solution or suspension, under a condition known to those skilled in the art to incorporate a promoter compound into a zeolite. Because the methods for incorporating or impregnating a promoter compound into a zeolite a solid composition such as, for example, impregnation by incipient wetness method, are well known to

those skilled in the art, the description of which is also omitted herein for the interest of brevity.

The composition of the invention then can be, if desired, pretreated with a reducing agent before being used in a transalkylation or hydrodealkylation process for converting a hydrocarbon to an olefin and an aromatic hydrocarbon. The presently preferred reducing agent is a hydrogen-containing fluid which comprises molecular hydrogen (H_2) in the range of from 1 to about 100, preferably about 5 to about 100, and most preferably 10 to 100 volume %. The reduction can be carried out at a temperature, in the range of from about 250°C to about 800°C for about 0.1 to about 10 hours preferably about 300°C to about 700°C for about 0.5 to about 7 hours, and most preferably 350°C to 650°C for 1 to 5 hours. The treatment with a reducing agent can also be carried out in-situ in a reactor which is used for a hydrocarbon conversion process.

According to the third embodiment of the present invention, a process useful for converting a hydrocarbon or a hydrocarbon mixture to a mixture rich in olefins and C_6 to C_8 aromatic hydrocarbons comprises, consists essentially of, or consists of contacting a fluid stream comprising a hydrocarbon or hydrocarbon mixture which can comprise paraffins, olefins, naphthenes, and aromatic compounds with a catalyst composition under a condition sufficient to

effect the conversion of a hydrocarbon mixture to a mixture rich in olefins and C_6 to C_8 aromatic hydrocarbons or to enhance the weight ratio of olefins (ethylene and propylene) to the C_6 to C_8 aromatic compounds. The fluid stream can also comprise a diluent selected from the group consisting of carbon dioxide, nitrogen, helium, carbon monoxide, steam, hydrogen, and combinations of two or more thereof. The presently preferred diluents are nitrogen and carbon dioxide for they are readily available and effective. The catalyst composition can be the same as that disclosed in the first embodiment of the invention and can be produced by the second embodiment of the invention. The weight ratio of the diluent to the hydrocarbon is in the range of from about 0.01:1 to about 10:1, preferably about 0.05:1 to about 5:1, and most preferably 0.1:1 to about 2:1.

The term "fluid" is used herein to denote gas, liquid, vapor, or combinations thereof. The term "hydrocarbon" is generally referred to, unless otherwise indicated, as one or more hydrocarbons having from about 4 carbon atoms to about 30 carbon atoms, preferably about 5 to about 20 carbon atoms, and most preferably 5 to 16 carbon atoms per molecule. The term "enhance or enhanced" refers to an increased weight ratio of olefins to BTX employing the catalyst composition as compared to employing only a zeolite such as commercially available ZSM-5. Examples of a hydrocarbon include, but are

not limited to butane, isobutane, pentane, isopentane, hexane, isohexane, cyclohexane, heptane, isoheptane, octane, isooctane, nonane, decane, undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, butenes, isobutene, pentenes, hexenes, benzene, toluene, ethylbenzene, xylenes, and combinations
5 of any two or more thereof.

Any fluid which contains a hydrocarbon as disclosed above can be used as the feed for the process of this invention. Generally, the fluid feed stream can also contain olefins, naphthenes (cycloalkanes), or some aromatic compounds. Examples of suitable, available fluid feeds include, but are not
10 limited to, gasolines from catalytic oil cracking processes, pyrolysis gasolines from thermal cracking of saturated hydrocarbons, naphthas, gas oils, reformates, and combinations of any two or more thereof. The origin of this fluid feed is not critical. Though particular composition of a feed is not critical, a preferred fluid feed is derived from gasolines which generally contain more
15 paraffins (alkanes) than combined content of olefins and aromatic compounds (if present).

The contacting of a fluid feed stream containing a hydrocarbon with the catalyst composition can be carried out in any technically suitable manner, in a batch or semicontinuous or continuous process, under a condition
20 effective to convert a hydrocarbon to a C_6 to C_8 aromatic hydrocarbon.

Generally, a fluid stream as disclosed above, preferably being in the vaporized state, is introduced into an aromatization reactor having a fixed catalyst bed, or a moving catalyst bed, or a fluidized catalyst bed, or combinations of any two or more thereof by any means known to one skilled in the art such as, for example, pressure, meter pump, and other similar means. Because an aromatization reactor and aromatization are well known to one skilled in the art, the description of which is omitted herein for the interest of brevity. The condition can include a weight hourly space velocity of the fluid stream in the range of about 0.01 to about 100, preferably about 0.05 to about 50, and most preferably 0.1 to 30 g feed/g catalyst/hour. Generally, the pressure can be in the range of from about 0 to about 1000 psig, preferably about 0 to about 200 psig, and most preferably 0 to 50 psig, and the temperature is about 250 to about 1000°C, preferably about 350 to about 750°C, and most preferably 450 to 650°C.

The process effluent generally contains a light gas fraction comprising hydrogen and methane; a C₂-C₃ fraction containing ethylene, propylene, ethane, and propane; an intermediate fraction including non-aromatic compounds higher than 3 carbon atoms; and a BTX aromatic hydrocarbons fraction (benzene, toluene, ortho-xylene, meta-xylene and para-xylene). Generally, the effluent can be separated into these principal

fractions by any known methods such as, for example, fractionation distillation. Because the separation methods are well known to one skilled in the art, the description of which is omitted herein. The intermediate fraction can be recycled to an aromatization reactor described above, methane, ethane, and propane can be used as fuel gas or as a feed for other reactions such as, for example, in a thermal cracking process to produce ethylene and propylene. The olefins can be recovered and further separated into individual olefins by any method known to one skilled in the art. The individual olefins can then be recovered and marketed. The BTX fraction can be further separated into individual C_6 to C_8 aromatic hydrocarbon fractions. Alternatively, the BTX fraction can undergo one or more reactions either before or after separation to individual C_6 to C_8 hydrocarbons so as to increase the content of the most desired BTX aromatic hydrocarbon. Suitable examples of such subsequent C_6 to C_8 aromatic hydrocarbon conversions are disproportionation of toluene (to form benzene and xylenes), transalkylation of benzene and xylenes (to form toluene), and isomerization of meta-xylene and/or ortho-xylene to para-xylene.

After the catalyst composition has been deactivated by, for example, coke deposition or feed poisons, to an extent that the feed conversion and/or the selectivity to the desired ratios of olefins to BTX have become unsatisfactory, the catalyst composition can be reactivated by any means known

to one skilled in the art such as, for example, calcining in air to burn off deposited coke and other carbonaceous materials, such as oligomers or polymers, preferably at a temperature of about 400 to about 650°C. The optimal time periods of the calcining depend generally on the types and amounts of deactivating deposits on the catalyst composition and on the calcination temperatures. These optimal time periods can easily be determined by those possessing ordinary skills in the art and are omitted herein for the interest of brevity.

The following examples are presented to further illustrate this invention and are not to be construed as unduly limiting the scope of the present invention.

EXAMPLE I

This example illustrates the preparation of catalyst composition of the invention.

A ZSM-5 zeolite obtained from UCI (United Catalysts, Inc., Louisville, Kentucky) having a product designation of T-4480 (obtained as a 1/16 inch extrudate) was used as control catalyst (catalyst A). Zeolite T-4480 contained 30 percent by weight of alumina as binder.

A ZSM-5 zeolite obtained from Chemie Uetikon AG, Uetikon, Switzerland having a product designation of Zeocat[®] PZ 2/50 H (obtained as powder) was used to produce other catalyst compositions.

5 First, the zeolite powder, following the addition of just enough water to make a paste, was extruded, to produce 1/16 inch extrudates which were calcined at 500°C for 3 hours (catalyst B).

Secondly, 5 g of the PZ 2/50H zeolite powder was mixed with 5 g of bentonite. Following the addition of just enough water to make a paste, the paste was extruded. The extrudates were heated to and at 500°C for 3 hours in a muffle furnace to produce 10 g of a zeolite containing clay (catalyst C).

10 In another preparation, powder PZ 2/50H zeolite (24 g) was mixed with 6 g of bentonite to form a mixture followed by the addition of just enough water to form a paste. The paste was then extruded, dried, and calcined at 500°C for 3 hours to produce 30 g of a zeolite containing 20 weight % clay (catalyst D).

15 Still in another preparation, 10 g of PZ 2/50H was mixed with 2 g of bentonite followed by the procedure described above for Catalyst C to produce 12 g of a zeolite containing 16.7 weight % clay (catalyst E).

20 In a separate run, 20 g of PZ 2/50H powder zeolite was thoroughly mixed with 5 g of bentonite. Following the procedure described

above for producing catalyst C, a zeolite (total 25 g) was produced (catalyst F) which contained 20 weight % clay by calculation.

Also in a separate run, 20 g of Zeocat zeolite PZ 2/50H was mixed with 5 g of stannous oxide and 5 g of bentonite to form a mixture.

5 Following the procedure described above for Catalyst C, a zeolite (catalyst G) (30 g) containing 16.7 weight % tin and 16.7 weight % clay was produced.

Still in a separate run, 20 g of PZ 2/50H powder, 5 g of diatomaceous earth, and 5 g of bentonite were thoroughly mixed. Following the procedure described above for the production of catalyst C, a zeolite
10 (catalyst H) containing 14.7 weight % diatomaceous earth and 16.7 weight % clay was produced.

Catalyst AA was produced by first mixing 18 g of PZ 2/50H powder, 7 g of bentonite, 0.6 g of zinc titanate, and enough water (21 ml) to make a paste. The paste was extruded to 1/16 inch extrudates. Following
15 drying the extrudates at 500°C for 3 hours, the extrudates were placed in a U-tube and heated with steam at 650°C for 4 hours.

Catalyst BB was produced by first mixing 18 g of PZ 2/50H powder, 7 g of bentonite, 0.4 g of magnesium silicate, and enough water to make a paste. The paste was then extruded to 1/16 inch extrudates which were
20 dried and heated with steam as above.

Catalyst CC was produced by first mixing 18 g of PZ 2/50H powder, 7 g of bentonite, 0.6 g of zinc titanate, 0.5 g of magnesium silicate, and 21 ml of H₂O to make a paste. The paste was extruded, dried, and heated with steam, as disclosed above for preparing catalysts AA and BB.

5 Catalyst DD was produced by first mixing 18 g of PZ 2/50H zeolite powder with 7 g of bentonite, 0.4 g of zinc orthosilicate, and 21 ml of water to make a paste. The paste was extruded, dried, and steamed as disclosed above for producing catalyst AA.

Catalyst EE was produced as follows. First, 36 g of PZ 2/50H
10 zeolite was mixed with 14 g of bentonite, 0.8 g of zinc orthosilicate, and 47.5 ml of water to make a paste. Secondly, the paste was extruded, dried, and heated with steam as disclosed above for catalyst AA production to produce a Zn/Si-incorporated zeolite. Thirdly, the Zn/Si-incorporated zeolite was mixed with a triethylphosphate (TEP) solution containing 1.2 g of TEP and 20 g of
15 n-hexane. The resulting mixture was left standing at about 20°C for one hour to produce P-incorporated zeolite. Finally, following removal of excess hexane by evaporation, the P-incorporated zeolite was calcined at 530°C for 3 hours. Catalyst DD contained 2 weight % phosphorus.

Catalyst FF was produced by the same produced described for catalyst EE except that the quantity of TEP used as 2.4 g. Catalyst FF contained 4 weight % phosphorus.

EXAMPLE II

5 This example illustrates the use of the catalyst compositions described in Example I as catalysts in the conversion of hydrocarbons to olefins and BTX.

A quartz reactor tube (inner diameter 1 centimeter; length 60 centimeter) was filled with a 20 centimeter bottom layer of Alundum® alumina (inert, low surface area alumina), 4.4 grams of one of the catalysts in the middle 20 centimeter of the tube, and a 20 centimeter top layer of Alundum® alumina. The liquid feed was an FCC-cracked gasoline obtained from Phillips Petroleum Company, Bartlesville, Oklahoma, and contained hydrocarbons shown in Table I. The liquid feed shown in Table I is summarized as: 38.7 weight percent (%) lights (C_5 s and C_6 s); 1.3% benzene; 5.4% toluene; 8.1% C_8 aromatics; 38.9% nonaromatics in BTX boiling range; and 25.9% heavies (C_8+). The feed was introduced into the reactor at a rate of 12 ml/hour (8.95 g/hour). The reaction temperature was 600°C and the reaction was carried out under atmospheric pressure.

The reactor effluent was cooled and separated into a gaseous phase and a liquid phase by passing through a wet ice trap for liquid product collection and then through a wet test meter for gas volume measurement. The liquid was weighed hourly and analyzed on a Hewlett-Packard 5890 gas chromatograph equipped with a fused silica column (DB-1). The gas was sampled hourly after the ice trap and analyzed on a Hewlett-Packard 5890 gas chromatograph using a HP-PLOT/ Al_2O_3 column. The gas was also analyzed for hydrogen content on a Carle gas chromatograph using hydrocarbon trap followed by a 13X molecular sieve column. Both phases were analyzed by gas chromatographs at intervals of about 1 hour. The results of the runs at about 6 hours are shown in Table II below which illustrates the production of olefins and BTX from the Table I feed and individual catalyst compositions produced in Example I.

Table I						
Hydrocarbon Analysis of Catalytically Cracked Gasoline						
	n-paraffins	Isoparaffins	Aromatics	Naphthenes	Olefins	Total
C ₁	0.000	0.000	0.000	0.000	0.000	0.000
C ₂	0.000	0.000	0.000	0.000	0.000	0.000
C ₃	0.000	0.000	0.000	0.000	0.000	0.000
C ₄	0.000	0.000	0.000	0.000	0.018	0.018
C ₅	1.292	8.147	0.000	0.169	10.741	20.348
C ₆	0.749	7.164	1.266	1.972	7.135	18.287
C ₇	0.740	4.576	5.354	2.746	6.483	19.899
C ₈	0.760	3.234	8.120	2.531	0.830	15.475
C ₉	0.187	2.070	8.187	0.708	0.125	11.278
C ₁₀	0.163	1.193	5.155	0.072	0.048	6.631
C ₁₁	0.153	0.307	3.606	0.191	0.000	4.257
C ₁₂	0.115	0.974	0.768	0.088	0.000	1.946
C ₁₃	0.048	0.000	0.000	0.000	0.000	0.048
C ₁₄	0.000	0.000	0.000	0.000	0.000	0.000
Total	4.208	27.664	32.457	8.478	23.381	98.188
					Total C ₁₅ +	0.108
					Total Unknowns:	1.704

Olefins and BTX Production (weight percent in product)

	Product yield (wt%)					
Catalyst	C ₂ ⁼	C ₃ ⁼	BTX	Total	% Coke	<u>Olefin</u> BTX
A (T4480)	6.4	6.8	42	54.7	4.4	.31
B (PZ 2/50H)	6.6	8.5	38	53.1	4.9	.40
C (PZ 2/50H + clay)	7.0	12.0	26	46.0	ND	.77
D (PZ 2/50H + clay)	9.8	8.9	41	59.7	1.7	.46
E (PZ 2/50H + clay)	6.6	5.4	44	56.0	1.2	.39
F (PZ 2/50H + clay)	7.8	6.8	42	56.6	1.2	.35
G (PZ 2/50H + clay + SnO)	4.4	11.8	35	51.2	0.4	.46
H (PZ 2/50H + clay + diatomaceous earth)	9.2	12.9	30	52.1	0.8	.74
AA(PZ 2/50H + clay + ZnTiO ₃)	7.0	14.2	34	55.2	0.44	.62
BB (PZ 2/50H + clay + MgSiO ₃)	7.0	13.6	27	47.6	0.6	.76
CC (PZ 2/50H + clay + ZnTiO ₃ + MgSiO ₃)	7.2	13.8	37	58.0	0.2	.54
DD (PZ 2/50H + clay + Zn ₂ SiO ₄)	7.8	11.8	40.5	60.1	0.28	0.48
EE (PZ 2/50H + clay + Zn ₂ SiO ₄ + TEP)	6.9	14.1	35.1	56.1	0.15	0.60
FF (PZ 2/50H + clay + Zn ₂ SiO ₄ + TEP)	5.2	13.4	24.9	43.5	0.24	0.75

The WHSV (weight hourly space velocity) of gasoline feed for each run was 2; coke was determined at the end of the reaction by removing the catalysts from the reactor and determined with a thermal gravimetric analyzer (TGA), manufactured by TA Instruments, New Castle, Delaware; ND, not determined; TEP, triethylphosphate.

Table II shows that commercial ZSM-5 zeolite (catalyst A) containing alumina binder had a high coke yield in a gasoline aromatization reaction. Table II also shows that a ZSM-5 zeolite (catalyst B) which did not contain alumina binder also had a high coke yield. Addition of a bentonite clay at various concentrations (catalysts D to F) significantly lowered the amount of coke yield. Table II further shows that increasing the ratio of zeolite to clay decreased the ratio of olefins to BTX in the product stream (catalysts C and D). The results presented in Table II further demonstrate that a zeolite containing clay and either stannous oxide (catalyst G) or diatomaceous earth (catalyst H) not only significantly further reduced the coke formation but also increased the ratio of olefins to BTX. Furthermore, Table II shows that incorporation of ZnTiO_3 (catalyst AA), MgSiO_3 (catalyst BB), or both ZnTiO_3 and MgSiO_3 (catalyst CC) also significantly improved the production of olefins and reduced coke formation. Finally, Table II shows that incorporation of Zn_2SiO_4 (catalyst DD), or both Zn_2SiO_4 and phosphorus (catalyst EE had 2 weight % P and catalyst FF contained 4 weight % P), had profound effect on reduction of coke formation in an aromatization process.

EXAMPLE III

This example illustrates another embodiment of the invention.

A Zeocat zeolite (catalyst I) containing about 70 weight % PZ 2/50H zeolite and 30% clay binder was a commercially available product
5 obtained as 1/16 inch extrudates.

Catalyst I (164 g) was mixed with 164 g of 37 weight % HCl and 164 g of water to make a suspension. The suspension was heated to and at 90°C for 2 hours to produce a heated suspension. Following the removal of aqueous phase by decantation from the suspension, the solid was washed with a
10 running tap water for about 30 minutes and then dried at 125°C for 2 hours. The dried solid was then calcined in air in a muffle furnace at 500°C for 4 hours to produce 158.58 g of an acid-leached clay-bound ZSM-5 (catalyst J).

A portion (50 g) of catalyst J was steamed (20 ml H₂O/hr) at 650°C in a U-shape tube for 8 hours to produce an acid-leached (AL)-steamed
15 zeolite (catalyst K).

In a separate run, 200 g of catalyst I was steamed as described immediately above to produce a steamed zeolite. The steamed zeolite (44 g) was added to a flask containing 44 ml of H₂O and 52 ml of HCl to produce a suspension. The suspension was heated to and then at 90°C for 2 hours.
20 Following removal of the aqueous phase by decantation, the solid was washed

with running tap water for about 30 minutes. The washed solid was dried in an oven at 125°C for 3 hours followed by calcination in a muffle furnace at 500°C for 3 hours to produce 40.54 g of steam and acid-leached zeolite (catalyst L).

The above catalysts I, J, K, and L were employed in a gasoline aromatization process for converting gasoline to olefins and BTX using the procedure disclosed in Example II. The purity of BTX was determined by dividing the area % of BTX in a GC chromatogram by the area % of all products in the same GC chromatogram. The results are shown in Table III below.

10

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Table III						
	Product (weight %)					
Catalyst	C ₂ ⁼	C ₃ ⁼	BTX	Purity	Ratio Olefins/BTX	% Coke
I (PZ 2/50H + clay)	7.3	9.2	36	97	0.46	5.6
J (AL-catalyst I)	8.1	7.3	40	97	0.39	1.1
K (AL-steam-catalyst I)	10.0	14.3	26	87	0.93	0.4
L (steam-AL-catalyst I)	10.6	13.3	30	94	0.80	0.4
AL, acid-leached; AL-steam; acid-leaching followed by steam treatment; steam-AL; steam treatment followed by acid-leaching.						

Table III shows that commercially available PZ 2/50 H zeolite probably also contained (contaminated with) some alumina binder which could

be removed by acid-leaching. The results in Table III also show that acid-leaching substantially decreased coke formation (catalyst J). Table III also shows that the coke content was further reduced and the ratio of olefins to BTX was further enhanced by an acid, steam, or both, treatment. Finally, Table III shows that the treatments of zeolite catalyst described in the invention did not adversely affect the BTX purity.

EXAMPLE IV

This example further illustrates the preparation of several catalyst materials containing a ZSM-5 zeolite, a zinc compound and a binder.

Catalyst M (control) was a silica-bound ZSM-5 catalyst containing about 30 weight % SiO_2 . This material was prepared by mixing 14.0 grams of a powdered ZSM-5 zeolite (provided by Chemie Uetikon AG, Uetikon, Switzerland, under the product "Zeocat[®] PZ 2/50H") with 15.0 grams of an aqueous colloidal solution of silica (containing about 40 weight % silica; a product of E.I. DuPont de Nemours and Company; marketed by Aldrich Chemical Company, Milwaukee, WI, under the product designation "Ludox[®] AS-40" colloidal silica). This mixture was dried at 120°C for about 3 hours and calcined in air at 520°C for about 3 hours. The calcined material was crushed and sieved. A 10-20 mesh fraction was treated with steam (flow rate: 6.8 ml/hour H_2O) at 650°C for 6 hours.

Catalyst N (invention) was a catalyst containing a ZSM-5 zeolite, silica binder and zinc aluminate (ZnAl_2O_4). This catalyst material was prepared by mixing 28.0 grams of PZ 2/50H zeolite powder, 1.12 grams of zinc aluminate and 30.0 grams of "Ludox[®] AS-40". This mixture was dried, calcined, crushed, and sieved as above for catalyst M and steam-treated in accordance with the procedure described for Catalyst AA. Catalyst B contained about 1 weight % zinc.

Catalyst O (invention) was a catalyst containing a ZSM-5 zeolite, silica binder and zinc orthosilicate (Zn_2SiO_4). This catalyst was prepared by mixing 28.0 grams of PZ 2/50H zeolite powder, 0.68 grams of zinc orthosilicate and 30.0 grams of Ludox[®] AS-40. This mixture was dried, calcined, crushed, sieved and steam-treated in accordance with the procedure described for Catalyst N. Catalyst O contained about 1 weight % zinc.

Catalyst P (invention) was a catalyst containing a ZSM-5 zeolite, zinc orthosilicate, boron oxide, and silica binder. This catalyst was prepared by mixing 20.0 grams of PZ 2/50H zeolite powder, 0.4 gram of zinc orthosilicate, 0.4 grams of boron oxide (B_2O_3) and 28 ml of Ludox[®] AS-40". This mixture was dried, calcined, crushed, sieved and steam-treated at 650°C for 4 hours essentially in accordance with the procedure described for Catalyst N. Catalyst P contained about 0.7 weight % zinc and about 0.4 weight % boron.

Catalyst Q (invention) was a catalyst containing a ZSM-5 zeolite, silica binder and zinc titanate. This catalyst was prepared by mixing 28.0 grams of PZ 2/50H zeolite powder, 0.99 gram of zinc titanate (ZnTiO_3), and 30.0 grams of Ludox[®] AS-40. The mixture was dried, calcined, crushed, sieved and steam-treated in accordance with the procedure described for Catalyst N. Catalyst Q contained about 1 weight % zinc.

Catalyst R (control) was a catalyst containing a ZSM-5 zeolite, alumina binder (in lieu of silica which was used in Catalysts M through Q, described above) and zinc titanate. Catalyst R was prepared by mixing 28.0 grams of PZ 2/50H, 1.00 gram of zinc titanate (ZnTiO_3) and 41.0 grams of an aqueous solution containing 50 weight % aluminum chlorhydrol ($\text{Al}_2(\text{OH})_5\text{Cl}$). This mixture was dried, calcined, crushed, sieved and steam-treated in accordance with the procedure described for Catalyst N. Catalyst Q contained about 1 weight % zinc and about 30 weight % alumina binder.

Catalyst S (control) was a catalyst containing a zinc-impregnated ZSM-5 catalyst and silica binder. This catalyst was prepared by soaking 10 grams of Catalyst M with an aqueous solution containing 0.5 gram of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 15 ml water at room temperature for about 1 hour. This Zn-impregnated material was dried, calcined, crushed, sieved and steam-treated in accordance with the procedure described for Catalyst N.

These catalyst compositions described in this Example were used in the conversion of hydrocarbons to olefins and BTX using the procedure described in Example II. The results are shown in Table IV below.

Table IV						
Olefins and BTX Production (weight percent in product)						
	Product yield (wt%)					
Catalyst	Ethylene	Propylene	BTX ^a	Total	<u>Olefin^b</u> BTX	% Coke ^c per Hr.
M (Control)	8.6	16.3	22.1	47.0	1.13	0.22
N (Invention)	7.7	13.1	37.8	58.6	0.55	0.27
O (Invention)	8.0	12.4	40.4	60.8	0.51	0.24
P (Invention)	8.3	10.5	44.4	63.2	0.42	0.17
Q (Invention)	8.3	11.2	45.1	64.6	0.43	0.24
R (Control)	8.1	11.8	40.1	60.0	0.50	1.5
S (Control)	7.1	9.2	45.6	62.0	0.36	0.63
^a Benzene + toluene + xylenes. ^b Weight ratio of (ethylene + propylene) to BTX. ^c Weight of coke on used (spent) catalyst at the end of a test run divided by the number of hours of the test run and multiplied by 100; weight of coke was determined with a thermal gravimetric analyzer (TGA), manufactured by TA Instruments, New Castle, Delaware.						

Test data in Table IV clearly show the advantages of invention Catalysts N, O, P and Q containing ZSM-5, a zinc compound (zinc aluminate or zinc orthosilicate or zinc titanate) and silica binder over control Catalyst M (without zinc), control Catalyst R (containing ZSM-5, zinc titanate and alumina

binder), and control Catalyst S (prepared by impregnation with a zinc compound). The invention catalysts attained a combination of high yield of desirable products (ethylene, propylene and BTX aromatics) and a low yield of coke (which will deactivate a catalyst). Control Catalyst M exhibited a low coking tendency but attained an unacceptably low (olefin + BTX) product yield, whereas control Catalyst R (containing alumina binder instead of silica binder) and control Catalyst S (prepared by impregnation of a ZSM-5 zeolite with a solution of zinc nitrate) produced coke at unacceptably high levels. Only invention Catalysts N-Q satisfied both requirements: high yield of C₂ and C₃ olefins and BTX, and low coking rate.

The results shown in the above examples clearly demonstrate that the present invention is well adapted to carry out the objects and attain the ends and advantages mentioned as well as those inherent therein. While modifications may be made by those skilled in the art, such modifications are encompassed within the spirit of the present invention as defined by the disclosure and the claims.